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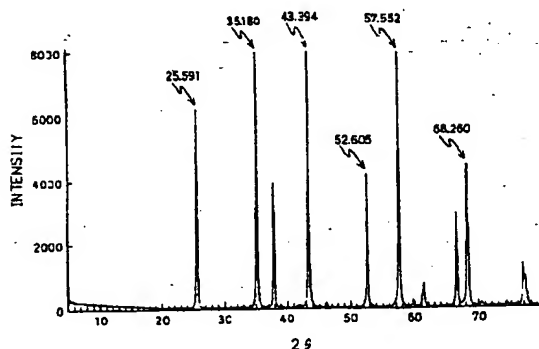
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(54) Title: ELASTOMER FORMED PRODUCT



(57) Abstract: A crosslinked fluorine-containing elastomer formed product which is prepared by crosslinking, by the use of a heat-resistant crosslinking agent, a crosslinkable fluorine-containing elastomer composition comprising a fluorine-containing elastomer such as a perfluoroelastomer having a crosslinking group such as a CN or COOH group and an inorganic filler having an average primary particle diameter of 5 μ m or less such as α -aluminum oxide or aluminum nitride. The crosslinked fluorine-containing elastomer formed product endures the use at a high temperature of 275°C or higher and also the irradiation of a high density plasma.

(57) Abstract:

To provide fluorine containing elastomer formed products which withstand used at high temperature of 275 °C or higher and withstand high density plasma. Crosslinked fluorine containing elastomer formed products which is obtained by crosslinking fluorine containing elastomer composition being formulated with organic filler such as α type aluminum oxide or aluminum nitride of primary mean particle size 5 μ m or less, in fluorine containing elastomer component such as perfluoro-elastomer having CN group or COOH group, with heat resistant crosslinking agent.

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- INTERNATIONAL SEARCH REPORT

For 2 character code and other abbreviations, refer to
"Guidance note for codes and abbreviations" described at
the top of each of periodically published *PCT* Gadget.

PATENT SPECIFICATION

Elastomer formed products

Technology Field

This invention concerns fluorine containing elastomer formed products which is excellent in good sealing property, use at high temperature exceeding 275 °C, especially thermal degradation is suppressed at continuous use in high temperature or use in temporarily high temperature, and property of high density plasma resistance, while maintaining working property (easiness of rubber kneading) and crosslinking property.

Technical Background

In a field of production of semiconductors, one of the most important objective is to avoid contamination with foreign object in fine powder shape being called as particles in the production process. This objective is also required for sealing materials such as O-rings which are used for seal of semiconductor production devices, for example. Therefore, making filler that is formulated in the elastomer formed product composing the sealing materials into super fine particles has been studied, because they are smaller than line distance (normally 0.2 μm or more) of micro patterns formed on semiconductor and would not short circuit the line by filling between lines, even if they get scattered out from the sealing material by a processing such as plasma irradiation, when super fine particles (primary mean particle size: 0.005 to 0.05 μm) are used.

Further, because of good plasma resistance (property of less weight loss and generation of particles under plasma irradiation environment), aluminum oxide filler has began to be adopted instead of carbon black which has been normally used in the field of semiconductor production devices (WO01/32782 pamphlet, for example).

Separate from above, processing at high temperature at 230 to 300 °C has been required recently with devices that are used for producing semiconductors. As an elastomer formed product that provides heat resistance at those high temperature, an elastomer composition for crosslinking has been proposed which is formulated with inorganic filler such as aluminum oxide being surface treated with silane type compound such as silane coupling agent (Patent Publication (Kokai) 2000-290454). According to this Publication, it describes that molding capability has been improved, however, there is no description about particle size and there is no description about usage. The silane type compound that has been used for the surface treatment may finally be a cause of contamination as impurity.

Further, compositions using titanium dioxide and aluminum oxide as fillers

have been proposed in Patent Publication 2000-502122, however, there is no description about particle size of the fillers being used, and its objective is not a prevention of generation of particles. Also, there is a problem that weight loss of formed products by plasma irradiation will be greater because titanium oxide is essential.

Furthermore, an elastomer composition for crosslinking being formulated with fine particle shape inorganic filler (primary mean particle size is about 0.005 to 0.05 μm) is described in WO01/32782 pamphlet, however, properties at 275 °C and above were not evaluated.

Generally in elastomer compositions for crosslinking, as the particle size of formulated inorganic filler gets smaller, its surface activity gets stronger and degrades the elastomer in the used at high temperature. Accordingly with the elastomer composition for crosslinking that is described in WO01/32782 pamphlet, the elastomer starts to degrade in a high temperature environment of 275 °C or higher and such as permanent compression strain becomes greater to reduce seal performance (later described Comparison examples).

Other than the above, formulating of aluminum oxide filler in 0.1 to 10 μm of mean particle size is described in Patent Publication Hei 1-118560, however, it is peroxide crosslink type which uses a crosslinking agent having no fluorine atom (TAIC) for crosslinking of the elastomer, its objective is not heat resistance and heat resistant elastomer formed products have not been obtained, either.

Further, a vulcanizing agent that improves heat resistance is shown as vulcanizing agent in Patent Publication 2000-154369, and there is a general description that metal oxide filler of particle size at 0.1 to 30 μm is formulated, however, concretely it uses metal oxide filler of 10 μm or larger and there is no teaching that heat resistance of elastomer formed products will change depending on type of filler, and of course there is no indication that heat resistance is good.

Further, these documents do not teach about what influence does inorganic filler has on high density plasma resistance, nor what type of filler will provide elastomer formed products having both plasma resistance and heat resistance.

Further, Kalrez 8475 and Kalrez 8575 (both are product names) made by DuPont Dow Elastomer Japan Co., Ltd. are known as seal materials being excellent in especially in heat resistance, however, weight loss by NF_3 plasma irradiation under a condition of severe plasma irradiation in this invention is 5.83 weight percent with Kalrez 8475 and 3.25 weight percent with Kalrez 8575, which do not satisfy required property of higher plasma resistance.

This invention has its objective to obtain formed products which do not thermally degrade at high temperature use and do not degrade by high density plasma irradiation, as well.

Disclosure of invention

This invention concerns elastomer formed products which are crosslinked

fluorine containing elastomer formed products being obtained by crosslinking a crosslinking fluorine containing elastomer composition which contains 0.5 to 100 weight parts of inorganic filler of primary mean particle size $0.5\ \mu\text{m}$ or less to 100 weight parts of fluorine containing elastomer component; permanent compression strain of the fluorine containing elastomer formed products under a condition of below described note (1) is 50 % or less, preferably 40 % or less and more preferably 30 % or less; and weight loss at NF_3 plasma irradiation under a condition of below described note (2) is 3 % or less, preferably 2 % or less.

Notes

Condition (1)

Sample: O-ring (AS-568A-214)

Test condition: Measure permanent compression strain at $275\ ^\circ\text{C}$ for 70 hours, according to JIS K6262-1997.

Condition (2)

Sample: O-ring (AS-568A-214)

Test equipment: ICP high density plasma device

This device takes following plasma parameters when O_2 gas volume is 16 SCCM, RF output is 800 W and pressure is 10 mTorr.

(Plasma parameters)

Electron temperature T_e : 4.54 eV

Electron density N_e : $5.81 \times 10^{10}\ \text{cm}^{-3}$

Ion density N_i : $1.14 \times 10^{11}\ \text{cm}^{-3}$

Saturation ion current I_i : $2.87\ \text{mAcm}^{-2}$

Plasma potential V_p : 27.76 V

Floating potential V_f : 11.42 V

Test condition:

NF_3 flow rate: 16 SCCM

Pressure: 10 mTorr

RF output: 800 W

Irradiation time: 30 minutes

Frequency: 13.56 MHz

As the crosslinking system, heat resistant crosslinking system, except for peroxide crosslinking system which uses only non-fluorine type crosslinking agent, is desired.

As the inorganic filler, those are desirable which contains at least one kind of inorganic filler containing aluminum, consists only of inorganic filler containing aluminum, contains at least one kind of inorganic filler essentially containing aluminum only as metal atom, or consists of inorganic filler essentially containing

aluminum only as metal atom.

As the inorganic filler, aluminum oxide filler, aluminum nitride filler and aluminum fluoride filler are especially desirable.

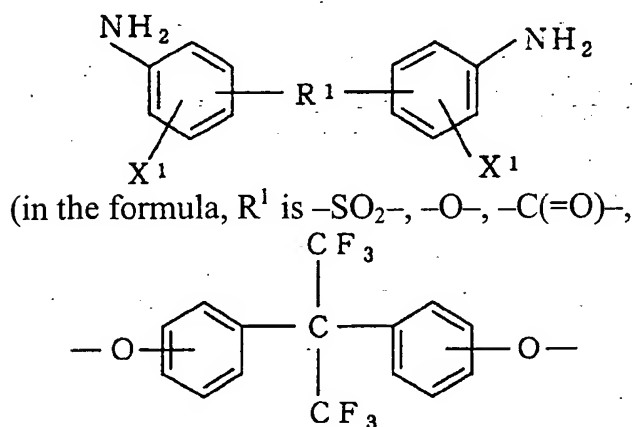
As more desirable aluminum oxide filler as the aluminum oxide filler, an aluminum oxide filler is mentioned wherein all six selected highest peaks (hereafter called as "major peaks") appearing in diffraction chart in a measurement of X-ray crystalline structure diffraction method are peaks having an origin of α type crystalline structure of aluminum oxide, especially all peaks appearing in diffraction chart in a measurement of X-ray crystalline structure diffraction method are essentially peaks having an origin of α type crystalline structure.

Desirable primary mean particle size of the inorganic filler is 1.0 μm or less and more desirably it is 0.2 μm or less.

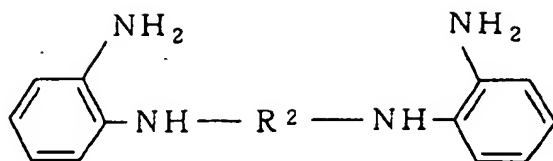
As the fluorine containing elastomer, per-fluoro elastomer having crosslinking groups, especially per-fluoro elastomer having crosslinking groups containing a structure unit having an origin of per-fluoro-olefin of carbon number 2 to 3, a structure unit having an origin of per-fluoro-vinyl-ether, and a structure unit having an origin of crosslinking group forming monomer, is desirable.

As the crosslinking group of the fluorine containing elastomer, CN group and/or COOH group are preferably mentioned.

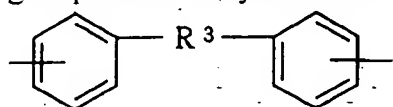
As the crosslinking agent that is used for the crosslinking fluorine containing elastomer, a compounds which is shown by Formula (1):



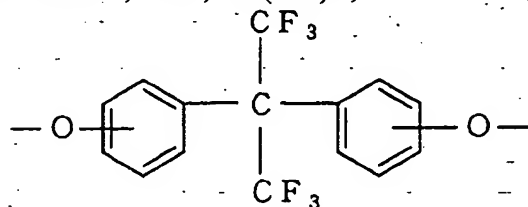
alkylidene group of carbon number 1 to 10, per-fluoro-alkylidene group of carbon number 1 to 10 or single bond and; X^1 are the same or different and are $-\text{OH}$, $-\text{NH}_2$, $-\text{SH}$, $-\text{NHR}$ (R is linear chain shape or branched chain shape alkyl group of carbon number 1 to 6 which may be substituted) or $-\text{NHAr}$ (Ar is phenyl group or naphthyl group which may be substituted)); a compound group which is shown by Formula (2):



(in the formula, R^2 is linear chain shape or branched chain shape alkylidene group, allylene group which may be substituted,

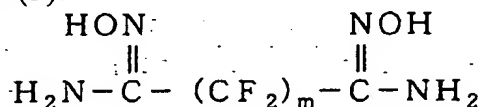


R^3 is $-\text{SO}_2-$, $-\text{O}-$, $-\text{C}(=\text{O})-$,



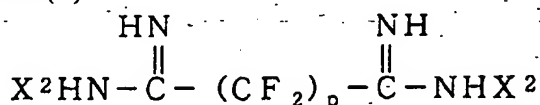
or single bond and;

a compound group which is shown by Formula (3):



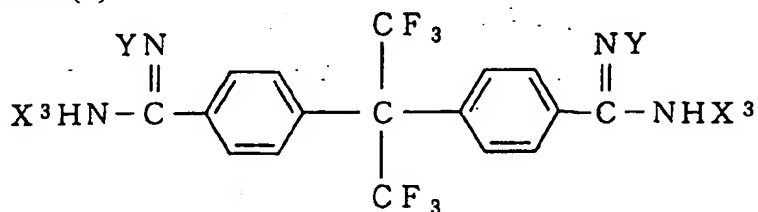
(in the formula, m is an integral number of 1 to 10);

a compound group which is shown by Formula (4):



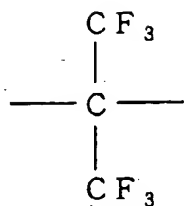
(in the formula, X^2 may be the same or different and H or NH_2 ; p is an integral number of 1 to 10); and/or

a compound group which is shown by Formula (5):

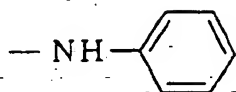


(in the formula, X^3 may be the same or different and are H or NH_2 ; Y may be the same or different and are H or OH), are preferably mentioned.

Especially a compound wherein R^1 in said Formula (1) is



and X¹ is



is desirable.

Further, it may contain tin compounds as the crosslinking promoter.

The elastomer formed products of this invention is especially effective when they are used for seals of production devices for semiconductors.

Brief description of illustrations

Figure 1 is X-ray crystalline structure diffraction chart of the aluminum oxide filler that is used in Embodiment example 1 of this invention and Comparison example 6.

Figure 2 is X-ray crystalline structure diffraction chart of the aluminum oxide filler that is used in Embodiment example 2 of this invention.

Figure 3 is X-ray crystalline structure diffraction chart of the aluminum oxide filler that is used in Embodiment example 3 of this invention.

Figure 4 is X-ray crystalline structure diffraction chart of the aluminum oxide filler that is used in Embodiment example 4 of this invention.

Figure 5 is X-ray crystalline structure diffraction chart of the aluminum oxide filler that is used in Comparison example 1 of this invention.

Figure 6 is X-ray crystalline structure diffraction chart of the aluminum oxide filler that is used in Comparison example 2 of this invention.

Figure 7 is X-ray crystalline structure diffraction chart of the aluminum oxide filler that is used in Comparison example 3 of this invention.

Figure 8 is X-ray crystalline structure diffraction chart of the aluminum oxide filler that is used in Comparison example 4 of this invention.

Figure 9 is X-ray crystalline structure diffraction chart of the aluminum oxide filler that is used in Comparison example 5 of this invention.

The best constitution for executing this invention

The elastomer formed products of this invention are to be obtained by crosslinking a crosslinking fluorine elastomer composition of inorganic filler having specific primary mean particle size and fluorine containing elastomer having crosslinking property in specific ratio, and it is defined by physical properties that permanent compression strain at high temperature (275 °C) is 50 % or less and weight loss at NF₃ plasma irradiation is 3 % or less.

As the organic fillers to be used, it is able to mention as examples such as, metal oxide filler such as titanium dioxide, silicon oxide, aluminum oxide and zinc oxide; sulfate filler such as barium sulfate and aluminum sulfate; carbonate filler such as barium carbonate; metal hydroxide filler such as aluminum hydroxide, nitride filler such as aluminum nitride and silicon nitride; fluoride filler such as aluminum fluoride and calcium fluoride; silicate filler such as aluminum silicate and calcium silicate; phosphate filler such as calcium phosphate and aluminum phosphate; borate filler such as aluminum borate; and carbide filler such as silicon carbide, aluminum carbide and calcium carbide; and among them, inorganic filler that contains only aluminum as metal atom is desirable, from the standpoint that it is superior in high density plasma resistance. As the examples of the inorganic filler that contain only aluminum as metal atom, it is able to mention tri-hydrogenated aluminum, aluminum oxide, aluminum sulfide, aluminum sulfite, aluminum sulfate, aluminum dithionate, aluminum sulfamate, aluminum selenide, aluminum selenite, aluminum selenate, aluminum telluride, aluminum tellurite, aluminum tellurate, aluminum fluoride, aluminum chloride, aluminum chlorate, aluminum per-chlorate, aluminum iodide, aluminum nitride, aluminum nitrate, aluminum phosphide, aluminum di-hydrogen-hypophosphite, aluminum hydrogen phosphite, aluminum hypo-phosphate, aluminum ortho-phosphate, aluminum hydrogen-phosphate, aluminum tri-hydrogen-phosphate, aluminum pyrophosphate, aluminum hydrogen-pyrophosphate, aluminum meta-phosphate, aluminum thio-phosphite, aluminum thio-hypo-phosphate, aluminum arsenide, aluminum arsenite, aluminum ortho-arsenate, aluminum pyroarsenate, aluminum ammonium hexa-fluoride, aluminum ammonium sulfate, aluminum ammonium selenate, aluminum hydrazinium sulfate, aluminum hydrazinium fluoride, and hydrates of these. Two or more kinds of these inorganic fillers may be used together within a range that would not ruin the objective of this invention, also one or more kinds of inorganic fillers that do not contain aluminum as atom may be used together, and one or more kinds of inorganic fillers that contain aluminum and at least one other metal atom may be used together.

Further, within a range that would not ruin the objective of this invention, inorganic filler that contains aluminum and at least one other metal atom may be used. As the examples of the inorganic filler that contain aluminum and at least one other metal atom, it is able to mention aluminum antimonide, aluminum bismuthate, aluminum bismuth bromide, aluminum lithium hydrogenate, lithium aluminate, lithium hydrogen aluminate, aluminum lithium nitride, aluminum tri-lithium hexa-fluoride, aluminum sodium hydride, sodium aluminate, aluminum sodium amide, aluminum tri-potassium hexa-fluoride, aluminum potassium chloride, aluminum potassium sulfate, aluminum potassium selenate, aluminum rubidium sulfate, aluminum rubidium hexa-fluoride, aluminum cesium hexa-fluoride, aluminum copper sulfate, aluminum silver sulfate, beryllium aluminate, aluminum magnesium hydride, magnesium aluminate, aluminum magnesium sulfate, calcium aluminate, strontium aluminate, barium aluminate, zinc aluminate,

aluminum zinc sulfate, cadmium aluminate, zeolite, and their hydride.

Two or more kinds of these inorganic fillers may be used together within a range that would not ruin the objective of this invention, and also one or more kinds of inorganic fillers that do not contain aluminum may be used together.

Further, inorganic fillers in fine particles are generally increased in surface activity such as various catalytic activities and adsorption activities than particles in large particle size because they are fine particles, and it is considered that making into fine particle will ruin heat resistance of elastomer itself and degrade it. Actually these phenomena may occur with many inorganic fillers, however, a fact was discovered by the inventors that the degrading phenomena related with surface activity do not occur unexpectedly with aluminum oxide filler, especially aluminum filler wherein the major peak that appear on diffraction chart when measured with X-ray crystalline structure diffraction method are all peaks originating from α type crystalline structure of aluminum oxide. There are such as α type, γ type, δ type and θ type for crystalline types of aluminum oxide, however, this phenomenon is only confirmed with α type.

This unusual phenomenon significantly appears especially with aluminum oxide filler wherein peaks that appear on diffraction chart when measured with X-ray crystalline structure diffraction method are essentially only peaks originating from α type crystalline structure of aluminum oxide. Where, "essentially only peaks originating from α type crystalline structure of aluminum oxide" means that apparent peaks originating from other crystalline types of aluminum oxide are not observed.

The peaks of α type crystalline of aluminum oxide which appear in diffraction chart when measured with X-ray crystalline structure diffraction method are observed as sharp forms at diffraction angles of 35 degrees, 43 degrees and 57 degrees as the major peaks, and further, small peaks are observed at diffraction angles of 25 degrees, 37 degrees, 52 degrees, 66 degrees and 68 degrees (later described Figures 1, 2 and 9). Further as the examples of "major peaks" are α type crystalline, later described Figure 3 and 4 are mentioned, for example. On the other hand, other crystalline types are small in peaks and broad (later described Figures 5 through 8) and able to be distinctively separated from α type.

On the other hand, a fact was discovered by the inventors that degradation phenomena related with surface activity do not occur with aluminum nitride filler, too.

Primary mean particle size of inorganic fillers that is represented by aluminum oxide is 5 μm or less, preferably 1.0 μm or less and more preferably 0.2 μm or less.

When they are used for elastomer formed products for the use of semiconductor production equipment, particle size should be smaller from the standpoint of reducing generation of so called particles. Lower limit is a range that is physically and chemically able to produce or grind, and it is normally mentioned to be around 0.001 μm .

As the fluorine containing elastomer which is the elastomer component of this

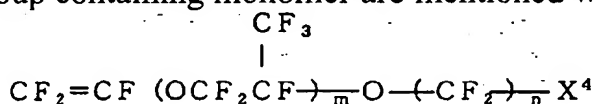
invention, per-fluoro-elastomer having crosslinking groups is desirable, and from the standpoint that it is excellent in mechanical strength; per-fluoro-elastomer comprising a structural unit of which origin is per-fluoro-olefin of carbon number 2 to 3, a structural unit of which origin is per-vinyl-ether, and a structural unit of which origin is monomer providing crosslinking groups, are especially desirable.

As the per-fluoro-olefin of carbon number 2 to 3, there are tetra-fluoro-ethylene (TFE) and hexa-fluoro-propylene (HEP); and TFE is desirable from the standpoint of good flexibility at low temperature. However, there is a case that HEP is further co-polymerized.

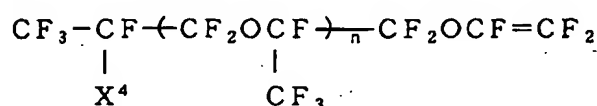
As the per-fluoro-vinyl-ether, a compound that is shown by $\text{CF}_2 = \text{CF} - \text{O} - \text{R}_f^1$ (R_f^1 is linear or branched linear per-fluoro-alkyl group of carbon number 1 to 8 or per-fluoro-oxy-alkyl group of carbon number 1 to 20) is desirable, and in concrete, it is able to mention per-fluoro-(alkyl-vinyl-ether) such as per-fluoro-(methyl-vinyl-ether), per-fluoro-(ethyl-vinyl-ether), per-fluoro-(propyl-vinyl-ether) and per-fluoro-(butyl-vinyl-ether); and per-fluoro-(alkoxyl-vinyl-ether) such as $\text{CF}_2 = \text{CFO}[\text{CF}_2\text{CF}(\text{CF}_2\text{O})_2\text{CF}_2\text{CF}_2\text{CF}_3$. Per-fluoro-(methyl-vinyl-ether) (PMVE) is especially desirable from the standpoint of good mechanical strength of formed parts.

As the crosslinking groups, it is able to mention such as carboxyl (COOH) group, alkoxyl carbonyl (COOR) group, nitrile (CN) group, iodine atom or bromine atom, and COOH group COOR group or CN group which are able to take heat resistant crosslinked structure when crosslinked are desirable, and especially COOH group or CN group are desirable which provide crosslinked structures having good heat resistance.

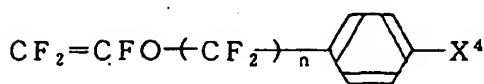
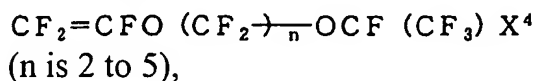
As the monomers that provide those crosslinking groups, such as nitrile group containing monomer, carboxyl group containing monomer and alkoxyl carbonyl group containing monomer are mentioned which are shown, for example, by;



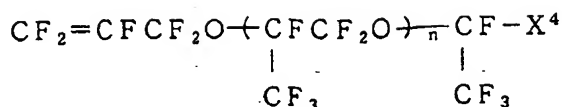
(in the formula, m is 0 to 5, n is 1 to 8),



(n is 1 to 4),

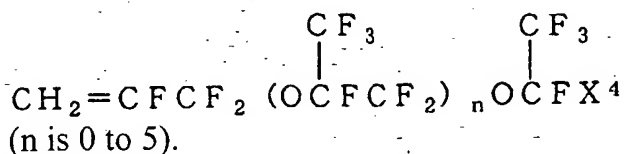


(n is 1 to 6),



(n is 1 to 5),

or



Among them, nitrile group containing monomer and carboxyl group containing monomer are desirable from the standpoints of good crosslinking reactivity and providing formed products with good heat resistance.

As concrete examples of these fluorine containing elastomers, following ones are mentioned as examples although they are not restricted.

(1) TFE / PMVE / $\text{CF}_2 = \text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$ (50 to 75 / 25 to 50 / 0.1 to 20 mole %).

This is desirable because it is good in crosslinking reactivity, and provides formed products with good heat resistance.

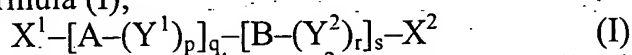
(2) TFE / PMVE / $\text{CF}_2 = \text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2(\text{CF}_3)\text{CN}$ (50 to 75 / 25 to 50 / 0.1 to 20 mole %).

This is desirable because it is good in crosslinking reactivity, and provides formed products with good heat resistance.

(3) TFE / $\text{CF}_2 = \text{CF}(\text{OCF}_2\text{CF}(\text{CF}_3))_2\text{OCF}_2\text{CF}_2\text{CF}_3$ / $\text{CF}_2 = \text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$ (60 to 85 / 15 to 40 / 0.1 to 20 mole %).

This is desirable because it is good in crosslinking reactivity, and provides formed products with good heat resistance and good low temperature flexibility.

As concrete examples of other fluorine containing elastomer being used for this invention, fluorine containing elastomer or segmented fluorine containing elastomer which are able to crosslink are desirable and which are shown by formula (I);



(in the formula, X^1 and X^2 may be arbitrarily changed by changing initiator or chain transfer agent at polymerization or modifying end group and not restricted within specific, however, both are the same or different and carboxyl group, alkoxyl carbonyl group, nitrile group, iodine atom, bromine atom or sulfonic acid are mentioned, for examples. Y^1 and Y^2 are the same or different and both are divalent organic group having carboxyl group, alkoxyl-carbonyl group or nitrile group on their side chain, A is elastomeric fluorine containing polymer chain segment, B is non-elastomeric fluorine containing polymer chain segment, p is an integral number of 0 to 50, q is an integral number of 1 to 5, r is an integral number of 0 to 10, s is an integral number of 0 to 3, where, one of X^1 , X^2 , Y^1 or Y^2 , nitrile group, carboxyl group or alkoxyl carboxyl group, and Y^1 and Y^2 may be randomly included in segments of A or B); and have carboxyl group, nitrile group and/or

alkoxyl carbonyl group as crosslinking point at the end of main chain and/or branched chain. This segmented fluorine containing elastomer is described in detail in WO99/24484 pamphlet and able to be applied to this invention too.

Said fluorine containing elastomer may be produced by polymerization methods such as emulsion polymerization method, suspension polymerization method and solution polymerization method.

As the polymerization initiator, those which is able to have a carboxyl group or a group that is able to generate carboxyl group (Acid fluoride, acid chloride and CF_2OH , for example. These all generate carboxyl group under existence of water.) existing at the end of elastomer, are preferably used. As the concrete examples, such as ammonium per-sulfate (APS) and potassium per-sulfate (KPS) are mentioned.

Normally used chain moving agent may be used for the adjustment of molecular weight, however, it is better not to use because the ratio of group that is able to generate carboxyl group being introduced at the end will be reduced. However, this is not applicable if the chain movement agent is those which enables said group at the end of elastomer. When the chain movement agent is not used, molecular weight may be adjusted by conducting polymerization at low pressure, less than 2 MPa·G, preferably less than 1 MPa·G. Other polymerization conditions shall not be restricted in specific, however, in order to obtain polymerization products having carboxyl group at the end and/or branched chain without applying acid treatment that is described later, it is desirable to adjust pH of polymerization to be 3 or less which is strong acidic.

Those which are thus obtained polymerization products may not contain free carboxyl group depending on polymerization condition, however, they are able to be converted to free carboxylic groups by applying following acid treatment.

The fluorine containing elastomer that is used in this invention is desired to be converted with groups of metal salt or ammonium of carboxylic acid which exist in the polymerization product into carboxylic group by applying an acid treatment to the polymerization products. As the acid treatment, washing with hydrochloric acid, sulfuric acid or nitric acid, or making the system of mixture after the polymerization to be less than pH 3 by these acid is appropriate.

These acid treatment is desired to be applied as a coagulating means when isolating the polymerization product from polymerization reaction mixture by coagulation, from the standpoint of simplifying the process. Or, the polymerization mixture may be acid treated and the polymerization product may be isolated by a means such as freeze drying. Further, it is able to adopt methods such as coagulation with such as ultrasound or coagulation with mechanical force.

Also carboxyl group may be introduced by oxidizing fluorine containing elastomer containing iodine or bromine with fuming sulfuric acid.

When the crosslinking group that is introduced into fluorine containing elastomer is COOH group or CN group, amount of crosslinking group is 0.1 mole % or more, preferably 0.2 to 5 mole % and more preferably 0.2 to 3 mole %, from

the standpoint of making crosslink density appropriate.

Formulated amount of inorganic filler is 0.5 to 150 weight parts to 100 weight parts of crosslinking fluorine containing elastomer, preferably it is 0.5 to 100 weight parts and more preferably it is 1 to 50 weight parts. If it is too little, the effect of addition of inorganic filler does not appear, and if it is too much, sealing capability of formed parts becomes less and hardness increases too.

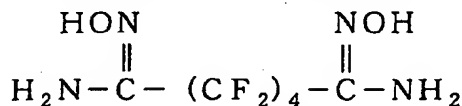
Crosslinking is available with various crosslinking systems in this invention, however, heat resistant crosslinking systems other than peroxide type crosslinking system which uses non-fluorine type crosslinking agent only, for improving heat resistance. As the "peroxide type crosslinking system which uses non-fluorine type crosslinking agent only" it is peroxide type crosslinking system using crosslinking promoter being represented by tri-aryl-isocyanurate (TAIC), for example, and peroxide crosslinking agent, and sufficient heat resistance is not obtained with this crosslinking system.

As crosslinking systems that provides especially good heat resistance, systems wherein the crosslinking group is COOH group or CN group using crosslinking agent which are shown in said formula (1) through (5) as crosslinking agent, are mentioned.

As the concrete examples of formula (1), such as 2,2-bis(3-amino-4-hydroxy-phenyl) hexa-fluoro-propane (general name: bis(amino-phenol) AF), 2,2-bis(3-amino-4-mercapto-phenyl) hexa-fluoro-propane, tetra-amino benzene, bis-3,4-di-amino-phenyl methane, bis-3,4-di-amino-phenyl ether, 2,2-bis(3,4-di-amino-phenyl) hexa-fluoro-propane, 2,2-bis[3-amino-4(N-methyl-amino)phenyl] hexa-fluoro-propane, 2,2-bis[3-amino-4(N-phenyl-amino)phenyl] hexa-fluoro-propane, 2,2-bis[3-amino-4(N-methyl-amino)phenyl] hexa-fluoro-propane, and 2,2-bis[3-amino-4(N-phenyl-amino)phenyl] hexa-fluoro-propane, are mentioned for examples.

As the concrete examples of crosslinking agent of formula (2), 2,2-bis[N-(2-amino-phenyl)-(3-amino-phenyl)] hexa-fluoro-propane and 2,2-bis[N-(2-amino-phenyl)-(4-amino-phenyl)] hexa-fluoro-propane are mentioned for examples.

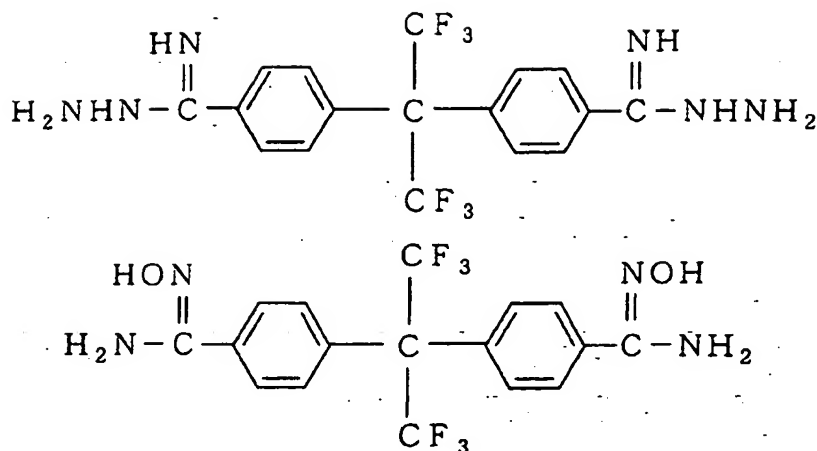
As the concrete examples of crosslinking agent of formula (3), such as



are mentioned for example.

As the concrete examples of crosslinking agent of formula (4), such as bis-amidorazone per-fluoro-adipate and bis-amidorazone per-fluoro-suberate are mentioned for example.

As the concrete examples of crosslinking agent of formula (5), such as



are mentioned for example.

Among them, crosslinking agents of formula (1) and formula (2), especially 2,2-bis[3-amino-4(N-phenyl-amino)phenyl] hexa-fluoro-propane (bisAF-PA), 2,2-bis[N-(2-amino-phenyl)-(3-amino-phenyl)] hexa-fluoro-propane, and 2,2-bis[N-(2-amino-phenyl)-(4-amino-phenyl)] hexa-fluoro-propane are desirable from the standpoint of improving heat resistance and chemical resistance of formed parts.

Formulating amount of crosslinking agent is preferably* 1 to 10 weight parts to 100 weight parts of elastomer, and preferably* it is 0.5 to 5 weight parts.

* *Translator's note: Word "preferably" is used twice and the first one should be mistakenly used and should be removed.*

Further, if it is necessary, crosslinking promoter may be formulated in place of the crosslinking agent or in addition to it. As the crosslinking promoter, such as organic tin compounds and organic and/or inorganic ammonium salts which generate ammonia gas at 120 to 225 °C, organic and/or inorganic compounds which generate ammonia gas at 40 to 330 °C, and ammonia that is adsorbed to inert carrier, are mentioned, for example. Where, when crosslinking promoter is used alone in place of crosslinking agent, the crosslinking system is triazine crosslinking system.

Formulating amount of crosslinking promoter is preferably* 0.01 to 10 weight parts to 100 weight parts of elastomer, and preferably* it is 0.01 to 5 weight parts.

* *Translator's note: Word "preferably" is used twice and the first one should be mistakenly used and should be removed.*

As the crosslinking agent, polyol crosslinking system may be used other than above described. Fluorinated tri-aryl-isocyanurate (F-TAIC, US4,320,216 and others), wherein hydrogen atoms of three aryl groups of tri-aryl-isocyanurate are substituted with fluorine atoms, is desirable as crosslinking agent from the standpoint of providing formed products superior in heat resistance, and when TAIC is used, the crosslinking system may be peroxide crosslinking system.

In this invention, ordinary additives, which are formulated to fluorine containing elastomer composition for crosslinking, such as filler, processing agent, plasticizer and colorant, for examples, may be formulated as needed, and one kind

ore more than that of ordinarily used crosslinking agent and crosslinking promoter which are different from above described may be formulated. Also, fluororubber that is known to the public may be mixed within a range that do not ruin the effect of this invention.

The crosslinking fluorine containing elastomer composition is prepared by mixing above described components with ordinary rubber processing equipment such as open rolls, banbury mixer and kneader, for example. Other than these, it is also able to prepare by a method to use enclosed mixer or a method to co-coagulate from emulsion mixing.

The method to obtain preformed product from above described composition may be ordinary method, and it is able to conduct with methods that are known to the public such as a method to heat and compress with metal mold, a method to inject into heated metal mold, and a method to extrude with an extruder. In case of extruded products such as hose and electric wire, it is able to use extruded preformed product without using crosslinking agent may be used as is. Of course it is able to use preformed products being applied with thermal crosslinking with such as steam by using crosslinking agent. Further, when it is a formed product such as O-ring and difficult to maintain the shape after releasing from the mold in un-crosslinked condition, it becomes possible to conduct by using preformed product being crosslinked in advance by using crosslinking agent.

This invention concerns thus obtained elastomer formed product.

The formed products of this invention have high mechanical strength and heat resistance. More than those and surprisingly, especially permanent compression strain, which is a standard for evaluating sealing property that is indispensable as sealing material, is reduced to 50 % or less, preferably 40 % or less and further 30 % or less even at temperature as high as 275 °C.

Also, plasma resistance is improved and it is able to control weight change within 3%, preferably within 2% when NF_3 is plasma irradiated at above described irradiation condition (2) on a formed product (O-ring: AS-568A-214) that has been washed then heated at 200 °C for 24 hours under nitrogen gas flow.

As the washing method, special washing methods being described in WO99/49997 pamphlet, for example, namely a method to wash with ultra-pure water, a method to wash with clean organic compound which is in liquid form at washing temperature or inorganic aqueous solution, a method to wash with dry etching, and a method to extract washing are preferably mentioned and by applying these washing treatment, formed parts for semiconductor production devices which is very highly cleaned and also with little outgas and superior in plasma resistance are obtained.

The fluorine containing elastomer formed products of this invention may be favorably used for formed products for producing semiconductor, especially semiconductor production devices which are required for high level of cleanliness, and especially for sealing materials for sealing semiconductor production devices wherein high density plasma irradiation is conducted. As the sealing materials,

such as O-rings, square rings, gaskets, packing, oil seals, bearing seals and lip seals are mentioned.

Other than above, it is able to be used as various elastomer products being used for semiconductor production devices, such as diaphragm, tube, hose and various rubber rolls. Further it may be used for lamination materials and lining materials.

Where, the semiconductor production devices being described in this invention are not restricted within devices that make semiconductors specific, but they broadly include general production devices which are used in the field of semiconductor such as production devices for liquid crystal panels and plasma panels wherein high level of cleanliness is required.

In concrete, following semiconductor production devices are mentioned as examples.

(1) Etching devices

Dry etching devices

Plasma etching device

Reactive ion etching device

Reactive ion beam etching device

Sputter etching device

Ion beam etching device

Wet etching devices

Ashing device

(2) Washing devices

Dry etching washing devices

UV/O₃ washing device

Ion beam washing device

Laser beam washing device

Plasma washing device

gas etching washing device

Extrusion washing devices

Soxhlet extraction washing device

High temperature high pressure extraction washing device

Microwave extraction washing device

Hypercritical extraction washing device

(3) Exposure device

Stepper

Coater-developer

(4) Polishing device

CMP device

(5) Film making device

CVD device

Sputtering device

(6) Diffusion, ion injection device

Oxidation diffusion device

Ion injection device

Embodiment examples

In the following, explanations are made by using embodiment examples, however, this invention shall not be restricted within those embodiment examples.

Where, the primary mean particle size and the diffraction chart by X-ray crystalline structure diffraction method in this embodiment examples and comparison examples were measured by following methods.

(Primary mean particle size)

Particle size is calculated from BET specific surface area s (m^2/g) and density of inorganic compound that composes the inorganic filler (g/cm^3) according to following equation. Where, it is assumed that the inorganic filler is in true spherical shape and particle diameter is uniform.

$$\text{Particle size (nm)} = 6 \times 10^3 / (d \times s)$$

Where, density of aluminum oxide is $3.9 \text{ g}/\text{cm}^3$, density of aluminum nitride is $3.05 \text{ g}/\text{cm}^3$, and density of titanium dioxide is $4.26 \text{ g}/\text{cm}^3$. For other inorganic compounds, general values such as values being described in Chemical Grand Dictionary (Kyoritsu Publishing), for example, are used.

(X-ray crystalline structure diffraction method)

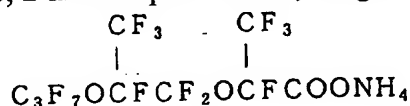
Measuring device: X-ray crystalline structure diffraction analyzer, RAD-RA (product name), made by Rigaku Denki Co., Ltd.

X-ray source: Cu-K α (modified to monochromatic with a monochromator)

Measurement range: $2\theta = 5$ to 80 degrees

Production example 1 (production of CN group containing fluorine containing elastomer)

In a autoclave of capacity 6 liter and made of stainless steel having no ignition source, 2 liter of pure water, 20 g of



as emulsifier, and 0.18 g of di-sodium hydrogen-phosphate 12 aqueous salt were charged, inside of the system was well substituted with nitrogen gas to deaerate, increased temperature to 50°C , then a mixed gas of tetrafluoroethylene (TFE) and per-fluoro(methyl-vinyl ether) (PMVE) (TFE / PMVE = 25 / 75 in mole ratio) was charged until inner pressure reached $0.78 \text{ MPa}\cdot\text{G}$, while mixing at 600 rpm. Then, 20 ml of water solution of ammonium per-sulfate (APS) at concentration of 527 mg/ml was injected using nitrogen pressure to initiate reaction.

At the point when interior pressure had reduced down to $0.69 \text{ MPa}\cdot\text{G}$ by the progress of reaction, 4.6 g of $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}(\text{CNVE})$ was injected using nitrogen pressure. Then 9.4 g of TFE and 10.6 g of PMVE were injected with their own pressures respectively so that pressure reaches $0.78 \text{ MPa}\cdot\text{G}$. After that, TFE and PMVE were similarly injected along with the progress of reaction to repeat pressure increase and decrease between 0.69 to $0.78 \text{ MPa}\cdot\text{G}$ and 4.6 g each of CNVE was injected with nitrogen pressure at the points when total of

TFE and PMVE reached 140 g, 260 g, 380 g and 500 g respectively.

After 20 hours from the initiation of polymerization reaction and at a point when total charge amount of TFE and PMVE had reached 600 g, the autoclave was cooled down, un-reacted monomers were discharged, and 2650 g of an aqueous dispersion of solid concentration 21.2 weight percent was obtained.

2400 g of this aqueous dispersion was diluted with 7200 g of water and slowly added into 5600 g of 3.5 weight percent aqueous hydrochloric solution. After mixing for 5 minutes after the addition, coagulated substance was filtered out, obtained polymer was further mixed into 4 kg of HCFC-141b, mixed for 5 minutes, and filtered again. Then this process of washing with HCFC-141b and filtering was further repeated for four more times, dried at 60 °C for 72 hours in vacuum, and 500 g of coagulant of CN group containing fluorine containing elastomer was obtained.

As a result of ^{19}F -NMR analysis, monomer unit composition of this elastomer was TFE / PMVE / CNVE = 59.1 / 40.0 / 0.9 mole %. This CN group containing perfluoroelastomer is called as "Elastomer A".

Production example 2 (Production of iodine containing fluorine elastomer)

In a autoclave of capacity 6 liter and made of stainless steel having not ignition source, 2 liter of pure water, 20 g of $\text{C}_7\text{F}_{15}\text{COONH}_4$ as emulsifier and 0.18 g of disodium hydrogen-phosphate 12 aqueous salt were charged, inside of the system was well substituted with nitrogen gas to deaerate, increased temperature to 50 °C, then a mixed gas of TFE and PMVE (TFE / PMVE = 27 / 73 in mole ratio) was charged until inner pressure reached 1.18 MPa·G, while mixing at 600 rpm. Then, 2 ml of water solution of ammonium per-sulfate (APS) at concentration of 186 mg/ml was injected using nitrogen pressure to initiate reaction.

At the point when interior pressure had reduced down to 1.08 MPa·G by the progress of reaction, 4.0 g of $\text{I}(\text{CF}_2)_4\text{I}$ which is iodine compound was injected using nitrogen pressure. Then 21.0 g of TFE and 21.0 g of PMVE were injected respectively so that presser reaches 1.18 MPa·G. After that, TFE and PMVE were similarly injected along with the progress of reaction. When total of TFE and PMVE reached 143 g, 511 g, 596 g and 697 g, 1.5 g each of $\text{ICH}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$, which is an iodine compound, was injected with nitrogen pressure at the points respectively, and 2 ml of 35 mg/ml of APS aqueous solution was injected with nitrogen pressure every 12 hours to keep the reaction continue, then the polymerization was stopped after 29 hours.

Obtained aqueous dispersion was frozen in dry ice/methanol to coagulate, the coagulant was washed with water after thawing, then vacuum dried, and 847 g of elastomer was obtained. Mooney viscosity ML1+10 (100 °C) of this elastomer was 58.

As a result of ^{19}F -NMR analysis, monomer unit composition of this elastomer excluding iodine containing monomer unit was TFE / PMVE = 62.9 / 37.1 mole %, and iodine content calculated from element analysis was 0.28 weight %. This iodine containing per-fluoro-elastomer is called as "Elastomer B".

Embodiment example 1

The CN group containing fluorine containing elastomer (Elastomer A), having carboxyl groups at ends being obtained in Production example, 1 2,2-bis[3-amino-4-(N-phenyl-amino)phenyl]hexa-fluoro-propane (Crosslinking agent A) that was synthesized by a method being described in Polymer Chemistry edition of Journal of Polymer Science, Vol. 20, pages 2381-2393 (1982), and aluminum oxide filler (AKP-50 (product name), Made by Sumitomo Chemical Industry Co., Ltd., Primary mean particle size: 0.15 μm , Crystalline type: essentially α type only, Refer to Figure 1) were mixed in a weight ratio of 100/4.25/15, and kneaded with open rolls to prepare fluorine containing elastomer composition that is able to crosslink.

After crosslinking this fluorine containing elastomer composition by pressing at 180 °C for 25 minutes, it was further oven crosslinked in a oven at 290 °C for 18 hours, and an O-ring test sample (AS-568A-214) was produced. Permanent compression strain and weight loss at NF_3 plasma irradiation was measured. The results are shown in Table 1.

(Permanent compression strain)

Permanent compression strain of O-ring (AS-568A-214) at 275 °C after 70 hours was measured according to JIS K6262-1997.

(Weight loss at NF_3 plasma irradiation)

Measurement device: ICP high density plasma device (Model RIE-101IPH, product name, made by Samco International Co., Ltd.)

Measurement condition (2):

NF_3 flow rate: 16 sccm

Pressure: 10 mTorr

RF output: 800 W

Irradiation time: 30 minutes

Frequency: 13.56 MHz

Washing treatment of test sample: Wash O-ring in substantially sufficient mixed solution of H_2SO_4 / H_2O_2 (6/4 weight ratio) at 100 °C for 15 minute under agitation, then wash with 5 % HF at 25 °C for 15 minutes, and further boiling wash with pure water at 100 °C for 2 hours and dry under nitrogen gas flow at 200 °C for 24 hours.

Irradiation operation: In order to stabilize atmosphere in the chamber of plasma irradiation device, discharge without object with actual gas was done for 5 minutes, as a chamber pre-processing. Then an aluminum container with test sample in it is placed at the center of RF electrode then plasma was irradiated under above described condition.

Weight measurement: Using an electronic analytical balance 2006MPE (product name) made by Sertorius GMBH, measure the order of 0.01 mg and round the digit of 0.01 mg.

Embodiment examples 2 through 5

Fluorine containing elastomers were prepared as same as Embodiment example

1 except for using those shown in Table 1 as the organic filler, and they were vulcanizing formed to produce O-rings (AS-568A-214).

Permanent compression strain and weight loss at NF_3 plasma irradiation were measured as same as Embodiment example 1 for produced O-rings. Results are shown in Table 1.

Organic fillers which were used in the Table 1 are as follows.

Fuller 1 (Embodiment example 1): Aluminum oxide filler (AKP-50 (product name) made by Sumitomo Chemical Industry Co., Ltd.. Primary mean particle size: 0.15 μm . Crystalline type: Essentially α type only. Refer to Figure 1.)

Filler 2 (Embodiment example 2): Aluminum oxide filler (TM-DAR (product name) made by Taimei Kagaku Co., Ltd.. Primary mean particle size: 0.11 μm . Crystalline type: Essentially α type only. Refer to Figure 2.)

Filler 3 (Embodiment example 3): Aluminum oxide filler (UA-5105 (product name) made by Showa Denko Co., Ltd.. Primary mean particle size: 0.15 μm . Crystalline type: Majority is α type. Refer to Figure 3.)

Filler 4 (Embodiment example 4): Aluminum oxide filler (UA-5205 (product name) made by Showa Denko Co., Ltd.. Primary mean particle size: 0.09 μm . Crystalline type: Majority is α type. Refer to Figure 4.)

Filler 5 (Embodiment example 5): Aluminum nitride filler (High purity aluminum nitride powder grade F (product name) made by Tokuyama. Primary mean particle size: 0.58 μm .)

Table 1

| | Embodiment examples | | | | |
|--|-----------------------|-----------------------|-----------------------|--------------------------|----------------------|
| | 1 | 2 | 3 | 4 | 5 |
| Fluorine containing elastomer | Elastomer A | Elastomer A | Elastomer A | Elastomer A | Elastomer A |
| Crosslinking agent | Crosslinking agent A | Crosslinking agent A | Crosslinking agent A | Crosslinking agent A | Crosslinking agent A |
| Inorganic filler | Filler 1 | Filler 2 | Filler 3 | Filler 4 | Filler 5 |
| Type | Aluminum oxide | Aluminum oxide | Aluminum oxide | Aluminum oxide | Aluminum nitride |
| Crystal type | (α type only) | (α type only) | (α type only) | (majority α type) | - |
| Diffraction chart | Figure 1 | Figure 2 | Figure 3 | Figure 4 | - |
| Mean primary particle diameter (μm) | 0.15 | 0.11 | 0.15 | 0.09 | 0.58 |
| Permanent compression strain (275 °C x 70 hr) | 20 % | 20 % | 18 % | 21 % | 17 % |
| Weight loss at plasma irradiation | 1.66 % | 1.65 % | 1.58 % | 1.60 % | 1.73 % |

Comparison examples 1 through 4

Fluorine containing elastomers were prepared as same as Embodiment example 1 except for using those shown on Table 2 as the aluminum oxide filler and 180 °C press crosslinking time in the time being shown on Table 2, and O-rings (AS-568A-214) were produced.

Each of produce O-rings were measured as same as Embodiment example 1, for permanent compression strain and weight loss at NF_3 plasma irradiation. Results are shown in Table 2.

Inorganic fillers which were used in Table 2 are as follows.

Filler 6 (comparison example 1): Aluminum oxide filler (AKP-G008 (product name) made by Sumitomo Chemical Industry Co., Ltd.. Primary mean particle size: 0.02 μm . Crystalline type: Major peaks are θ type. Refer to Figure 5.)

Filler 7 (comparison example 2): Aluminum oxide filler that was used in Comparison example 2 (AKP-G008 (product name) made by Sumitomo Chemical Industry Co., Ltd.. Primary mean particle size: 0.02 μm . Crystalline type: Major peaks are θ type.) Refer to Figure 5.) was sintered at 1100 °C for 3 hours. α type crystalline and θ type crystalline coexist as a mixture. (Refer to Figure 6.)

Filler 8 (comparison example 3): Aluminum oxide filler (TM-300 (product name) made by Taimei Kagaku Co., Ltd.. Primary mean particle size: 0.007 μm . Crystalline type: Main peaks are γ type. Refer to Figure 7.)

Filler 9 (comparison example 4): Aluminum oxide filler (Al_2O_3 -C (product name) made by Degussa-Huls. Primary mean particle size: 0.015 μm . Crystalline type: Main peaks are δ type. Refer to Figure 8.)

Comparison example 5

Fluorine containing elastomer containing iodine ends (Elastomer B) being obtained in Production example 2, Perhexa 25B (product name, made by Japan Oil and Fat Industry Co., Ltd.) as crosslinking promoter, tri-aryl-isocyanurate (TAIC) as crosslinking agent, and aluminum oxide filler (Filler 10, AO-802 (product name) made by Tatsumori Co., Ltd., primary mean particle size: 0.26 μm , crystalline type: essentially α type only, refer to Figure 9) were mixed in a weight ratio of 100/10/1/3, and kneaded with open rolls, and fluorine containing elastomer composition that is able to crosslink was prepared.

This fluorine containing elastomer composition was peroxide crosslinked under a condition of 160 °C, 10 minutes press crosslinking (primary crosslinking) and 180 °C, 4 hours oven crosslinking (secondary crosslinking), and an O-ring (AS-568A-214) test sample was made. Permanent compression strain and weight loss at NF_3 plasma irradiation of this test sample were measured as same as Embodiment example 1. Results are shown in Table 2.

Comparison example 6

Fluorine containing elastomer was prepared as same as Comparison example 5 except for using Filler 1 (aluminum oxide filler (AKP-50 (product name) made by Sumitomo Chemical Industry Co., Ltd., primary mean particle size: 0.15 μm , crystalline type: essentially α type only, refer to Figure 1.) as aluminum oxide

filler, and changing the mixing ratio of Elastomer B, Perhexa 25B, TAIC and aluminum oxide filler to be 100/1.5/4.0/15 (weight ratio), then it was vulcanizing formed and an O-ring (AS-568A-214) was made. Permanent compression strain and weight loss at NF_3 plasma irradiation of produced O-ring were measured as same as Embodiment example 1. Results are shown in Table 2.

Comparison example 7

Fluorine containing elastomer was prepared as same as embodiment example 1 except for using titanium dioxide filler (Filler 11, TM-1 (product name) made by Fuji Titan Industry Co., Ltd., crystalline type: rutile type, primary mean particle size: $0.28 \mu\text{m}$) in place of as aluminum oxide filler, and changing the mixing ratio of Elastomer A, Crosslinking agent A, and Filler 11 to be 100/2.8/23 (weight ratio), it was vulcanizing formed and an O-ring (AS-568A-214) was made. Permanent compression strain and weight loss at NF_3 plasma irradiation of produced O-ring were measured as same as Embodiment example 1. Results are shown in Table 2.

Table 2

| | Comparison examples | | | | | | |
|--|-----------------------|---|-----------------------|-----------------------|-----------------------|-----------------------|----------------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Fluorine containing elastomer | Elastomer A | Elastomer A | Elastomer A | Elastomer A | Elastomer B | Elastomer B | Elastomer A |
| Crosslinking agent | Crosslinking agent A | Crosslinking agent A | Crosslinking agent A | Crosslinking agent A | TAIC | TAIC | Crosslinking agent A |
| Crosslinking promoter | - | - | - | - | Parhexa 25B | Parhexa 25B | - |
| Inorganic filler | Filler 6 | Filler 7 | Filler 8 | Filler 9 | Filler 10 | Filler 1 | Filler 11 |
| Type | Aluminum oxide | Aluminum oxide | Aluminum oxide | Aluminum oxide | Aluminum oxide | Aluminum oxide | Titanium dioxide |
| Crystal type | (θ type only) | (mixture of α and θ type) | (γ type only) | (δ type only) | (α type only) | (α type only) | - |
| Diffraction chart | Figure 5 | Figure 6 | Figure 7 | Figure 8 | Figure 9 | Figure 1 | - |
| Mean primary particle diameter (μm) | 0.02 | 0.02 | 0.007 | 0.015 | 0.26 | 0.15 | 0.28 |
| Press crosslinking time (180 °C) | 25 min. | 25 min. | 160 min. | 130 min. | - | - | 25 min. |
| Permanent compression strain (275 °C x 70 hr) | 61 % | 57 % | 70 % | 83 % | 68 % | 63 % | 17 % |
| Weight loss at plasma irradiation | 1.65 % | 1.58 % | 1.71 % | 1.63 % | 2.17 % | 1.65 % | 5.98 % |

Probability of industrial application

According to this invention, it is able to provide formed products of fluorine containing elastomer which withstand use at high temperature higher than 275 °C and also withstand high density plasma.

CLAIMS

1. Elastomer formed product containing fluorine which is a fluorine containing elastomer product being crosslinked and obtained by crosslinking a crosslinking and fluorine containing elastomer composition that contains 0.5 to 100 weight parts of inorganic filler of primary mean diameter being 5 μ m or less to 100 weight parts of fluorine containing elastomer; and permanent compression strain of the elastomer formed product containing fluorine is 50 % or less under a condition of following note (1) and weight loss is 3 % or less at NF₃ plasma irradiation under a condition of following note (2).

Notes

Condition (1)

Sample: O-ring (AS-568A-214)

Test condition: Measure permanent compression strain at 275 °C for 70 hours, according to JIS K6262-1997.

Condition (2)

Sample: O-ring (AS-568A-214)

Test equipment: ICP high density plasma device

Test condition:

NF₃ flow rate: 16 SCCM

Pressure: 10 mTorr

RF output: 800 W

Irradiation time: 30 minutes

Frequency: 13.56 MHz

2. Elastomer formed product that is described in Claims 1 which is obtained by crosslinking with heat resistant crosslinking system other than peroxide crosslinking system that uses non-fluorine type crosslinking agent alone.
3. Elastomer formed product that is described in Claims 1 or 2 wherein the inorganic filler contains at least one kind of inorganic filler that contains aluminum.
4. Elastomer formed product that is described in Claims 1 or 2 wherein the inorganic filler comprises an inorganic filler alone that contains aluminum.
5. Elastomer formed product that is described in Claims 1 or 2 wherein the inorganic filler contains at least one kind of inorganic filler that essentially contains aluminum only as metal atom.
6. Elastomer formed product that is described in Claims 1 or 2 wherein the inorganic filler comprises an inorganic filler alone that essentially contains aluminum only as metal atom.
7. Elastomer formed product that is described in Claims 3, 4, 5 or 6 wherein the inorganic filler is aluminum oxide filler, aluminum nitride filler or aluminum fluoride filler.
8. Elastomer formed product that is described in Claim 7 wherein the inorganic

filler is aluminum oxide filler and all six selected highest peaks appearing in diffraction chart in a measurement of X-ray crystalline structure diffraction method are peaks having an origin of α type crystalline structure.

9. Elastomer formed product that is described in Claim 7 wherein the inorganic filler is aluminum oxide filler and all peaks appearing in diffraction chart in a measurement of X-ray crystalline structure diffraction method are essentially peaks having an origin of α type crystalline structure.

10. Elastomer formed product that is described in Claims 1, 2, 3, 4, 5, 6, 7, 8 or 9 wherein primary mean particle diameter of inorganic filler is 1.0 μm or smaller.

11. Elastomer formed product that is described in Claims 1, 2, 3, 4, 5, 6, 7, 8 or 9 wherein primary mean particle diameter of inorganic filler is 0.2 μm or smaller.

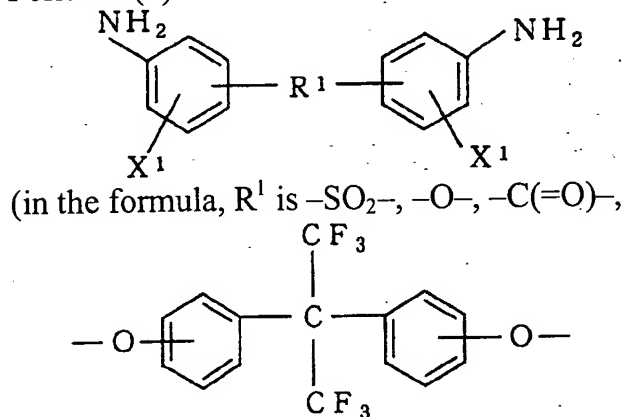
12. Elastomer formed product that is described in Claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11 wherein the fluorine containing elastomer is per-fluoro elastomer having crosslinking groups.

13. Elastomer formed product that is described in Claims 12 wherein the per-fluoro elastomer having crosslinking groups contain a structure unit having an origin of per-fluoro-olefin of carbon number 2 to 3, a structure unit having an origin of per-fluoro-vinyl-ether, and a structure unit having an origin of crosslinking group forming monomer.

14. Elastomer formed product that is described in Claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12 wherein the fluorine containing elastomer has CN group and/or COOH group as crosslinking group.

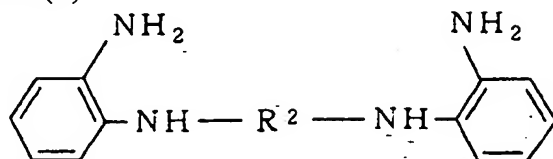
15. Elastomer formed product that is described in Claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 or 14 wherein said crosslinking fluorine containing elastomer composition is a composition containing; a compounds which is shown by

Formula (1):

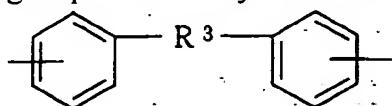


alkylidene group of carbon number 1 to 10, per-fluoro-alkylidene group of carbon number 1 to 10 or single bond band; X^1 are the same or different and are $-\text{OH}$, $-\text{NH}_2$, $-\text{SH}$, $-\text{NHR}$ (R is linear chain shape or branched chain shape alkyl group of carbon number 1 to 6 which may be substituted) or $-\text{NHAr}$ (Ar is phenyl group or naphthyl group which may be substituted));

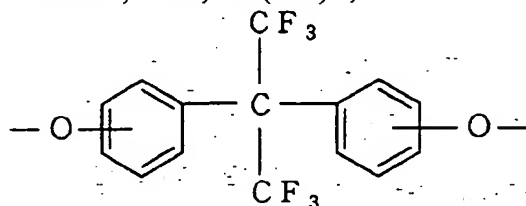
a compound group which is shown by
Formula (2):



(in the formula, R^2 is linear chain shape or branched chain shape alkylidene group, allylene group which may be substituted,

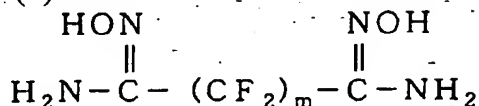


R^3 is $-\text{SO}_2-$, $-\text{O}-$, $-\text{C}(=\text{O})-$,



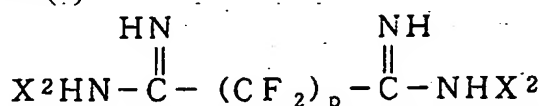
or single bond and;

a compound group which is shown by
Formula (3):



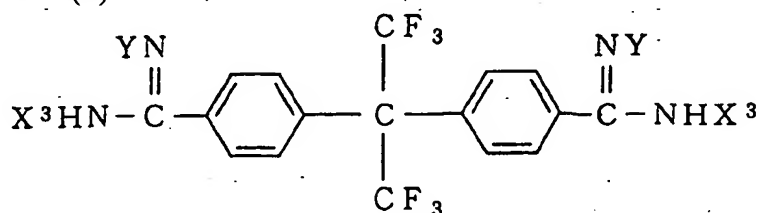
(in the formula, m is an integral number of 1 to 10);

a compound group which is shown by
Formula (4):



(in the formula, X^2 may be the same or different and H or NH_2 ; p is an integral number of 1 to 10); and/or

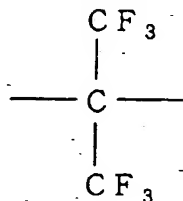
a compound group which is shown by
Formula (5):



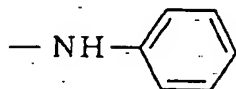
(in the formula, X^3 may be the same or different and are H or NH_2 ; Y may be the same or different and are H or OH).

16. Elastomer formed product that is described in Claim 15 wherein the

crosslinking agent is a compound wherein R¹ is



and X¹ is



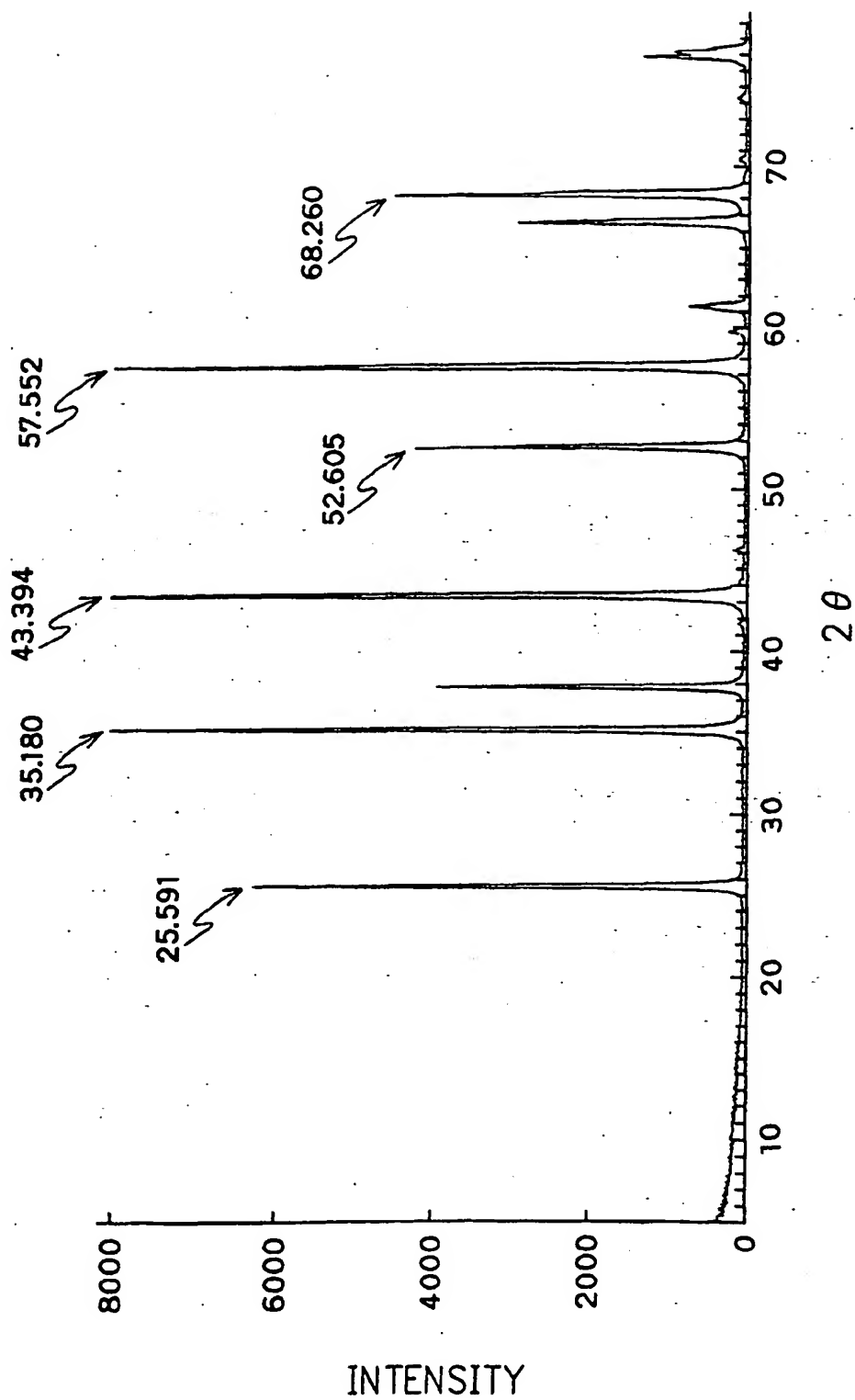
17. Elastomer formed products which are described in Claim 14 and contain organic tin compound as crosslinking promoter.

18. Elastomer formed products which are described in Claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16 or 17 and are used for seals of semiconductor-producing devices.

Translated by: Hideyo Sugimura 651-490-0233, hsugimura@pipeline.com, October 30, 2003

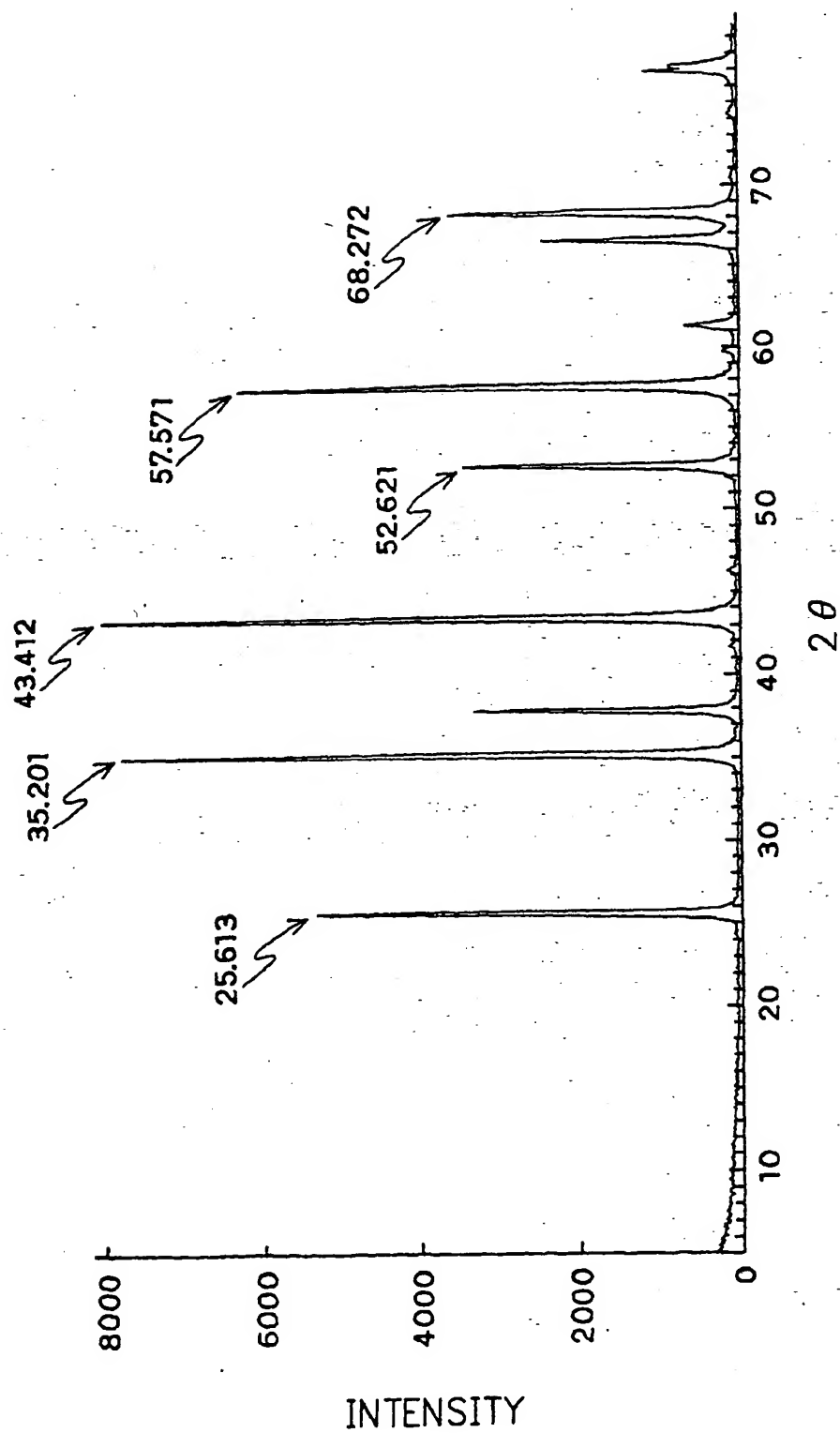
1/9

FIG. 1



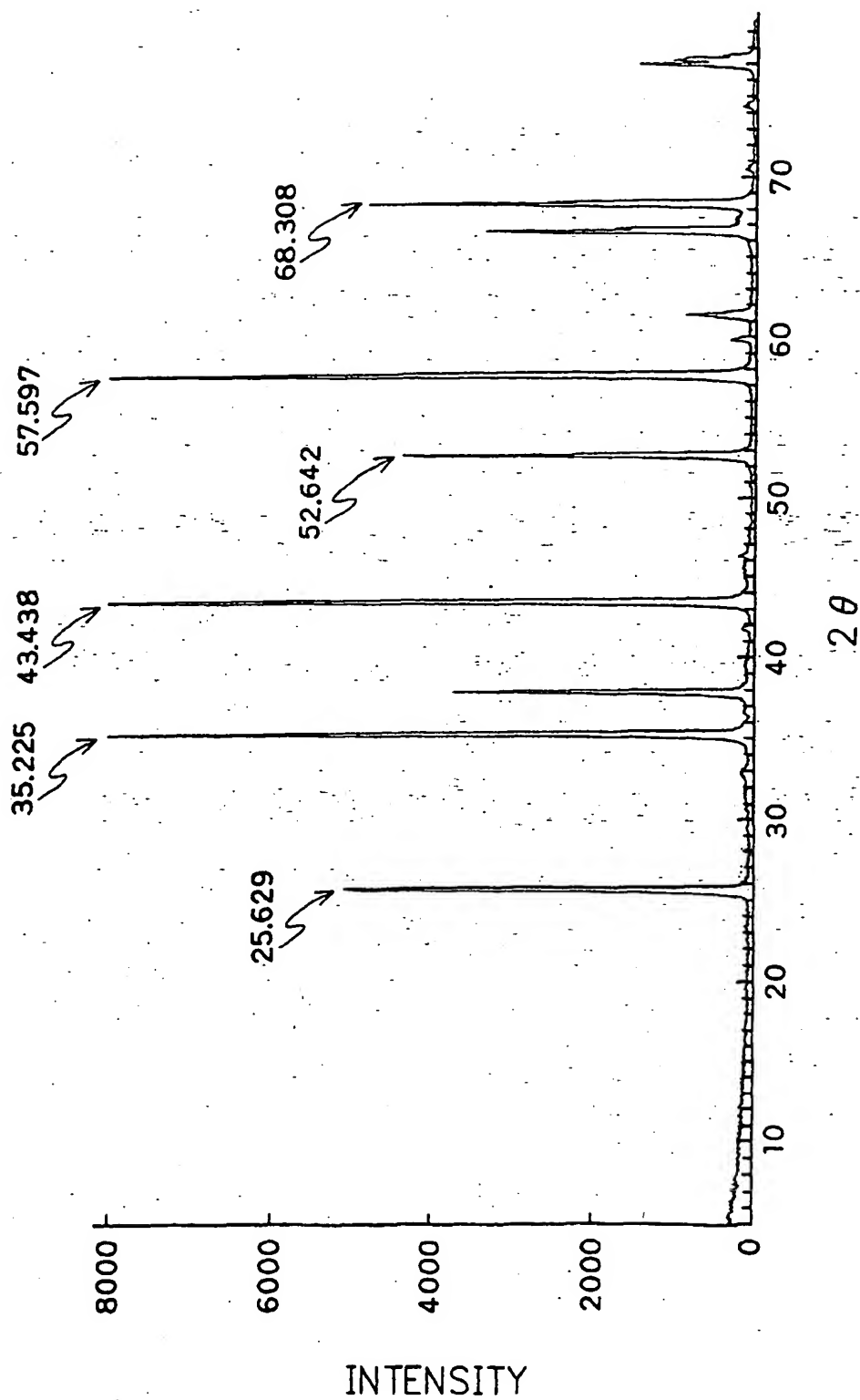
2/9

FIG. 2



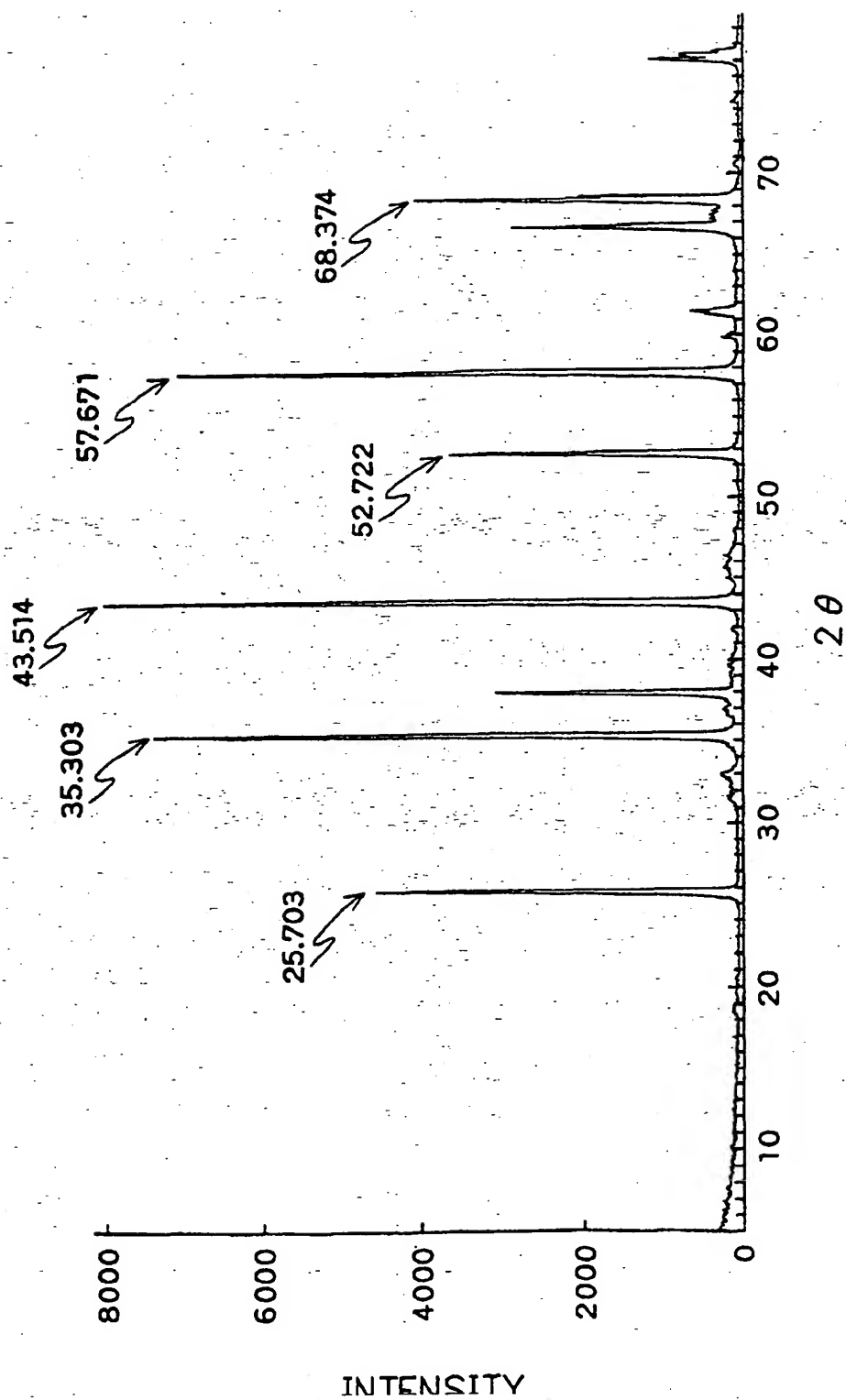
3/9

FIG. 3



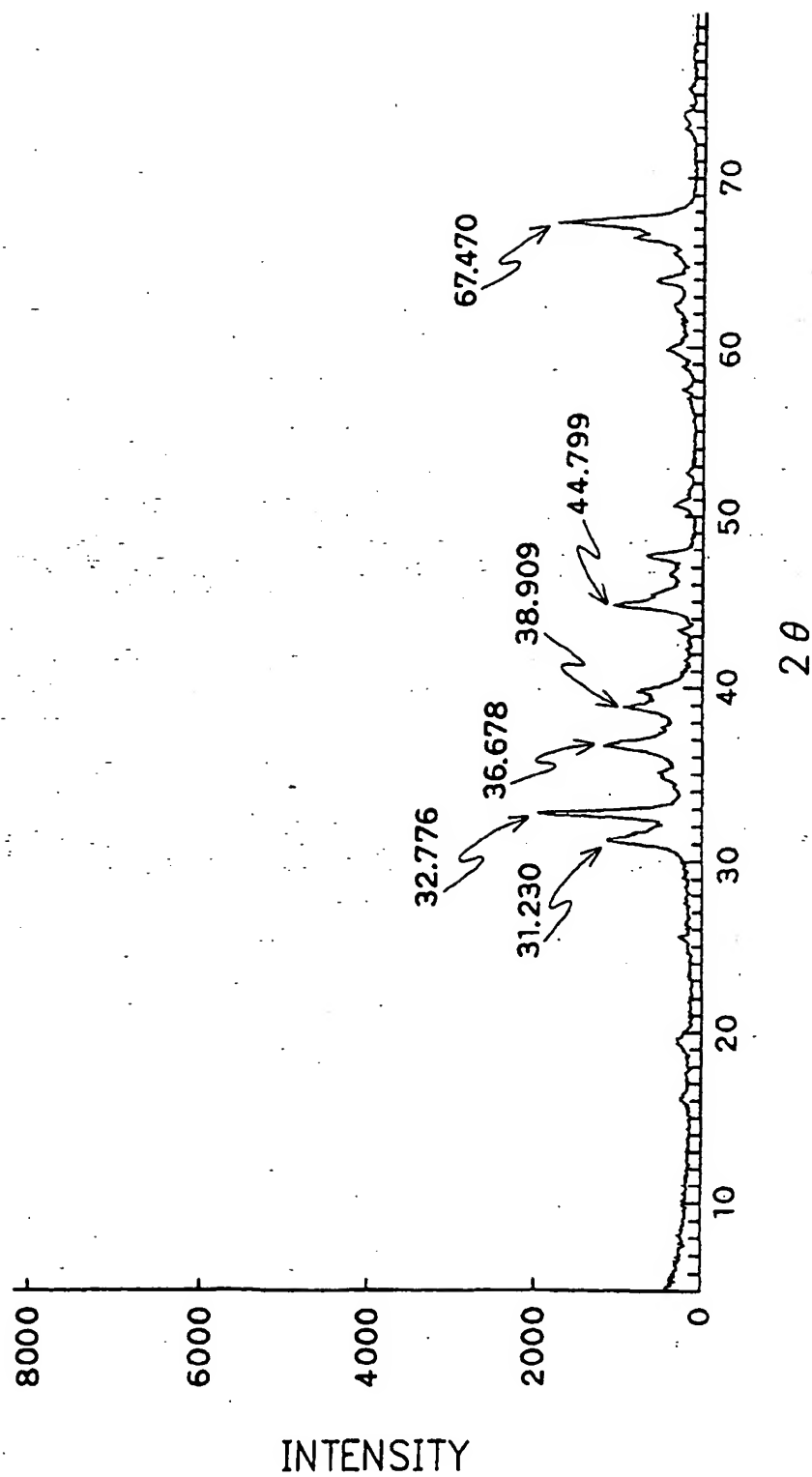
4/9

FIG. 4



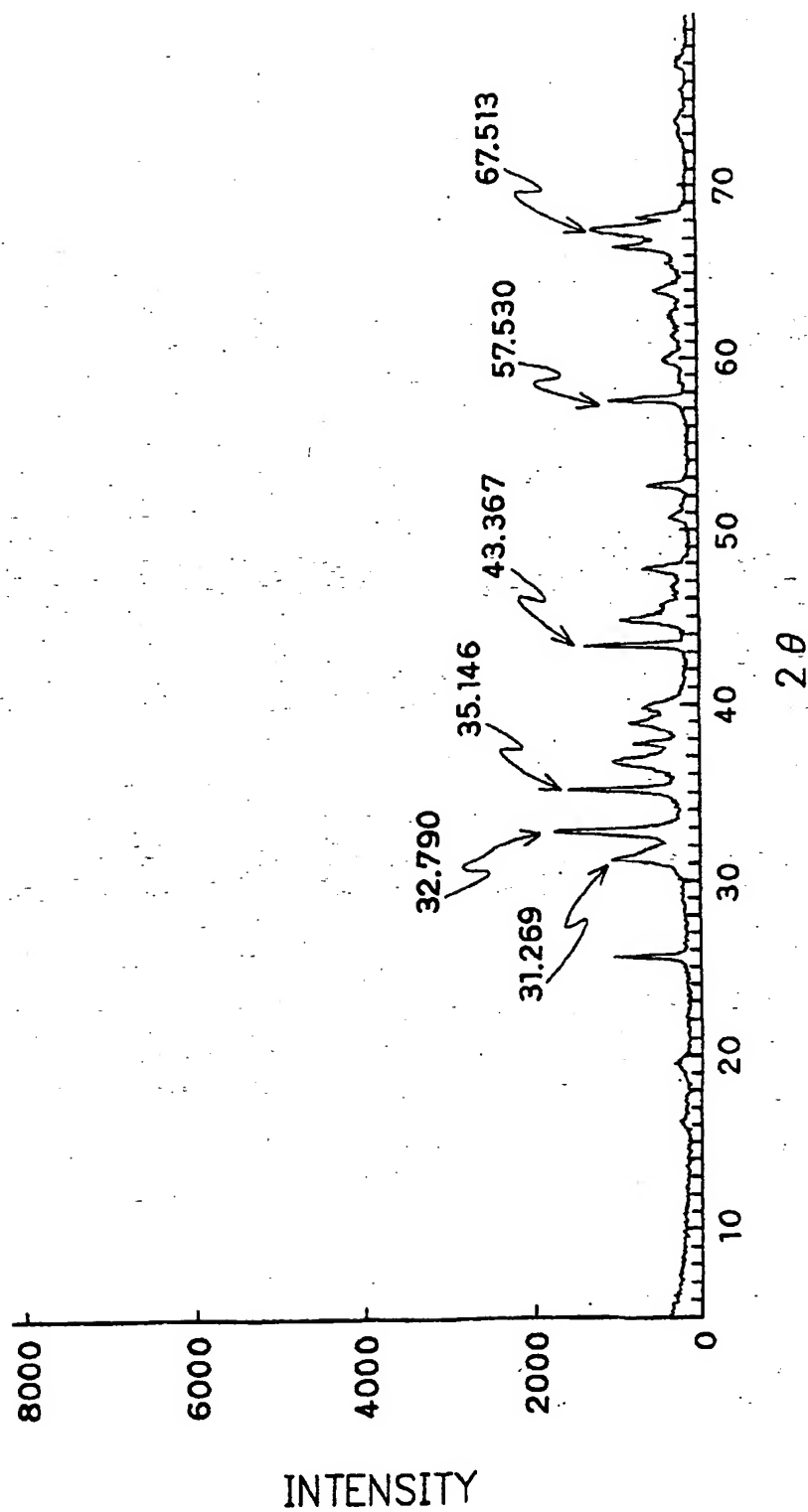
5/9

FIG. 5



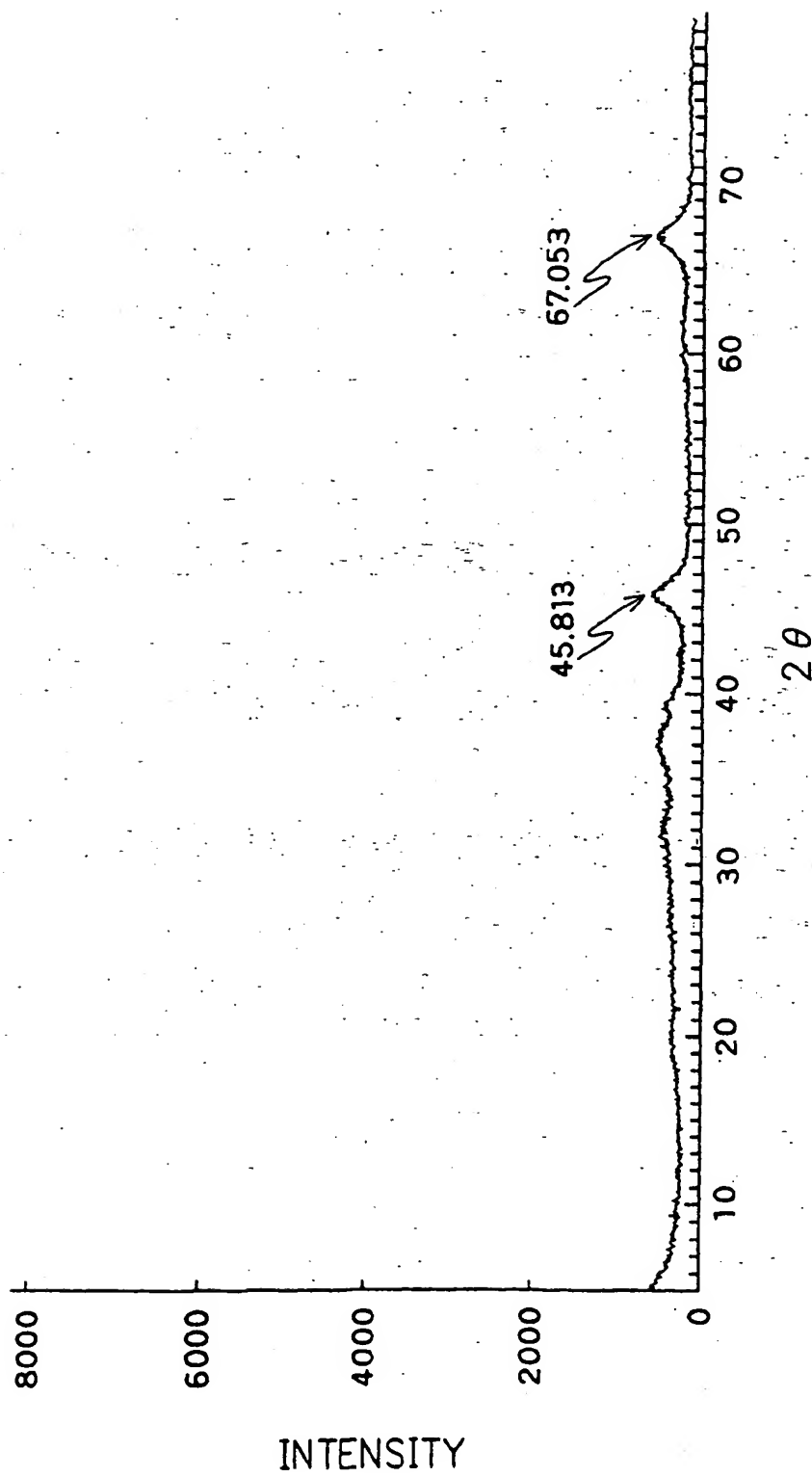
6/9

FIG. 6



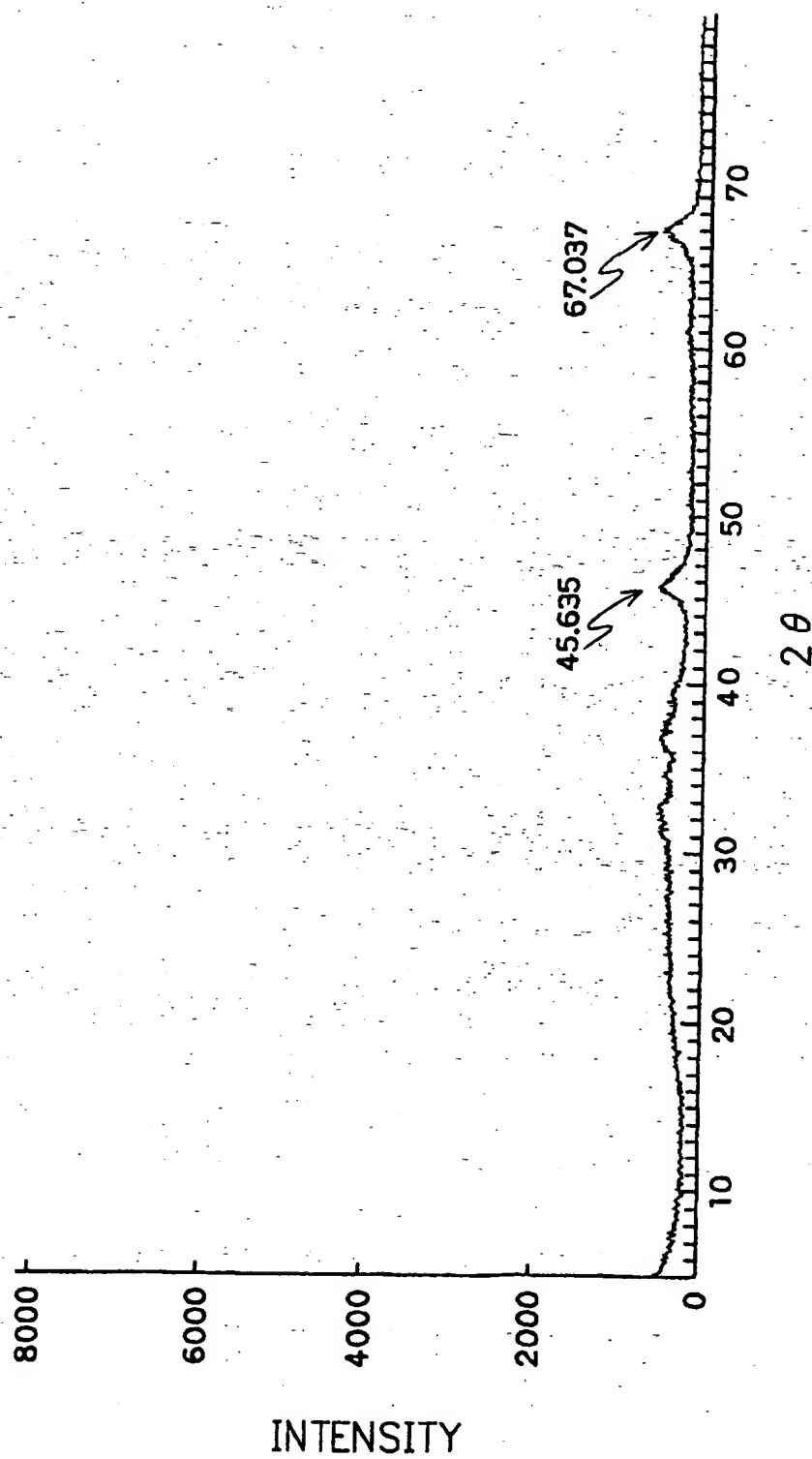
7/9

FIG. 7



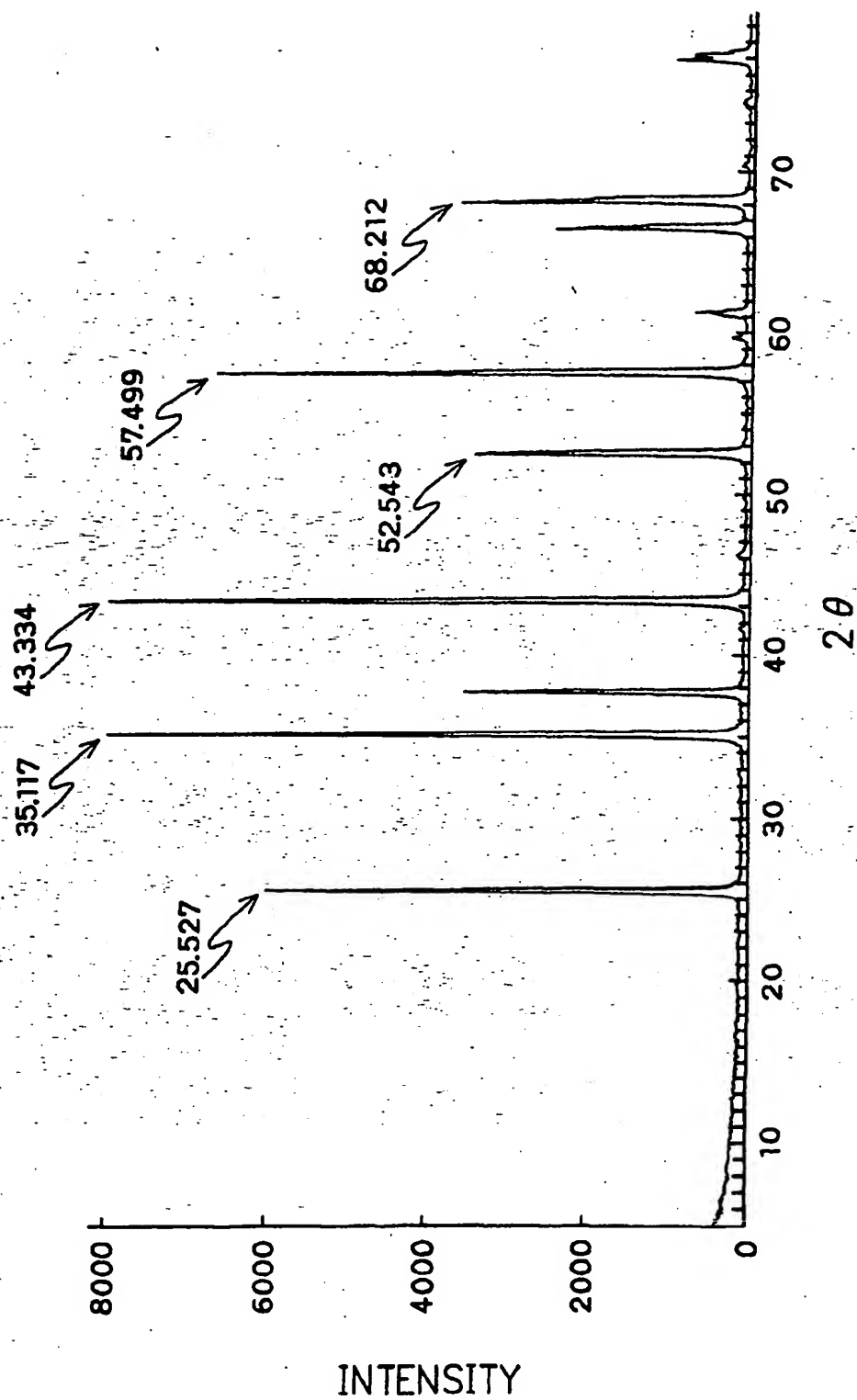
8/9

FIG. 8



9/9

FIG. 9



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